

Synthesis and characterization of magnetically separable

$\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ (Ni-Mg ferrite) catalyst for Knoevenagel reaction in water

Santosh L. Khillare, Aashish O. Dhokte, Machhindra K. Lande and Balasaheb R. Arbad*.

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra, India.

*Corresponding Author: E-Mail: abrchem9@gmail.com

ABSTRACT

An eco-friendly $\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ solid heterogeneous catalyst has been employed for the synthesis of 5-arylidene malonitrile derivatives *via* Knoevenagel condensation of various aromatic aldehydes and malonitrile in water at stirring condition. The catalyst was prepared by simple co-precipitation method and calcined at 550 °C. The calcined powder sample was characterized by XRD, FT-IR, SEM and EDS, TPD and BET techniques. The catalytic activity results suggest that, the methodology adopted to offer significant improvements in the synthesis of 5-arylidene malonitriles with regards to short reaction times, high yields and the catalyst was successfully reused for three cycles without significant loss of activity.

Keywords: Aromatic aldehyde, Malonitrile, $\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$, Heterogeneous catalysis, Ferrite.

1. INTRODUCTION

Conventionally, heterogeneous catalysis is preferential over homogeneous catalysis for a large number of applications in both fundamental research and industrial applications due to its ease of handling, simple workup, and regenerability. In view of environmental and economical aspects, there is an ongoing effort to replace the conventional catalysts by solid heterogeneous catalysts, this is mainly due to some advantages such as non toxicity, non-corrosiveness less expensive and easy to recover and reuse. Surface active metal oxides are generally used to prepare heterogeneous catalysts, however, the efficient separation and recycling of metal oxide catalysts is difficult and not economical, but when catalyst is magnetic in nature such as ferrite then it can be separated by a small magnet placed at the bottom of the reaction vessel [1]. Mixed oxides with spinel structure have several applications. They are known as pigments with high thermal chemical stability, thus suitable for coloring enamels and ceramics. Some spinel type compounds are also found to be excellent refractory, magnetic and catalytic materials [2], and photoelectric properties [3]. Considering these aspects, it is decided to study the catalytic role of Ni-Mg Ferrite.

Carbon- carbon bond formation reaction is one of the most important reactions in organic

synthesis. Knoevenagel condensation is one of such reaction between an aldehydes and active methylene compounds. Owing to its applicability in the synthesis of various chemicals and chemical intermediates [4] coumarin derivatives, cosmetics, perfumes and pharmaceuticals [5,6], fine chemical industry such as polymers [7], and synthesis of carbocyclic as well as heterocyclic compounds [8] of biological significance, many modifications have been made in this process in recent years using ionic liquids [9], Lewis acids such as CuCl_2 [10], ZnCl_2 [11] silica supported ammonium acetate [12] and so on have been reported in the literature. However, in most of these methods homogeneous conditions are used, expensive reagents are involved or a combination of several additives are employed.

In recent years inorganic solid acid catalyzed organic reactions are gaining much attention. In this work, we report the preparation and characterization of series of magnetically separable solid catalyst containing Ni (II), Mg (II) and Fe (III) with different molar ratios by simple co precipitation. The catalytic behavior of Ni-Mg Ferrite is studied in the synthesis of 5-arylidene malonitriles by the condensation of aromatic aldehydes and malonitrile using water as a solvent (Scheme 1). The catalyst/product(s) separation could be easily achieved with a permanent magnet and more than 99% of catalyst could usually be recovered from each reaction.

The catalyst was easily separated with an external magnet and the recovered catalyst was reusable without significant loss in the catalytic activity.

2. EXPERIMENTAL

2.1 Materials

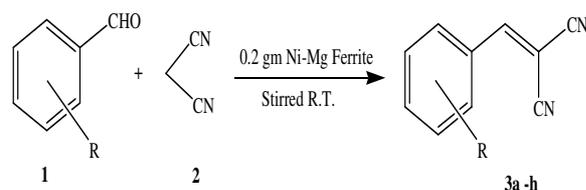
The entire chemicals used were of synthesis grade reagents (Merck) and used as received.

2.2. Catalyst preparation

In a typical reaction, stoichiometric amounts of iron (III) nitrate, nickel (II) nitrate and magnesium (II) nitrate were dissolved in deionized water. The pH of the solution was adjusted to 9 by the addition of aqueous ammonia, the solution was stirred vigorously for 4 h at 80°C and the precipitate was filtered, washed, and dried. Thus, the composite hydroxide of mixed metals so formed is calcined at 550°C for 5 hrs. After calcination $Ni_xMg_{1-x}Fe_2O_4$ is formed. The catalytic material was synthesized by varying composition of Ni (II) and Mg (II) such as (a) $x = 0.8$, (b) $x = 0.6$, (c) $x = 0.4$ and (d) $x = 0.2$.

2.3. Knoevenagel reaction: a typical procedure

In a typical reaction, aromatic aldehyde **1** (5mmol) and malononitrile **2** (5mmol) and synthesized Ni-Mg ferrite (0.2 gm) as catalysts in water (20 ml) was stirred (scheme 1) when reaction was completed as indicated by TLC, the catalyst was separated by magnet and dried for its next use and the reaction mixture was filtered. The crude product was purified by recrystallization from ethanol to give the corresponding pure compound **3**. The pure product was identified by IR, 1H -NMR and physical data (M.P.) and compared with those reported in the literature.



Scheme - 1: Synthesis of 5-arylidene malononitriles catalyzed by Ni-Mg Ferrite solid heterogeneous catalyst.

3a: IR (KBr) - 2220, 2922, 1587, 1485, 956, 673 cm^{-1} . 1H NMR (δ in DMSO), 7.24 (t, 1 H), 7.62 (d, 2 H), 7.78 (d, 2H), 8.02 (s, 1H).

3e: IR (KBr)- 2221, 1576, 1483, 1363, 850. 1HNMR (δ in DMSO) 7.45 (d, 2H), 7.78 (d, 2H), 7.86 (s, 1H).

3. RESULTS AND DISCUSSION

3.1. Characterization of synthesized Ferrite

The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 advance X-ray diffractometer using Cu $K\alpha$ radiation with a wavelength of 0.154056 nm. To study the surface morphology of synthesized ferrite scanning electron microscopy (SEM) analyses were carried out with a JEOL JSM-6330 LA operated at 20.0kV and 1.0nA. The elemental composition of the metals in the synthesized ferrite was examined using an energy dispersive spectrophotometer (EDS). BET surface area has been measured by means of N_2 adsorption at 77.68 K performed on a micromeritics ASAP 2010 and temperature programmed desorption of ammonia (NH_3 -TPD) measurements were carried out on a micromeritics chemisoft TPx V1.02.

3.2. XRD analysis.

The powder X-ray diffraction pattern of Ni-Mg ferrite calcined at 550 °C for 5 hrs is shown in figure 1. While analyzing XRD pattern, it is observed that there are slight differences between the relative intensities and width of reflexes, which indicates the differences of crystallite size. The sharp peaks represents that all Ni-Mg ferrites are crystalline in nature.

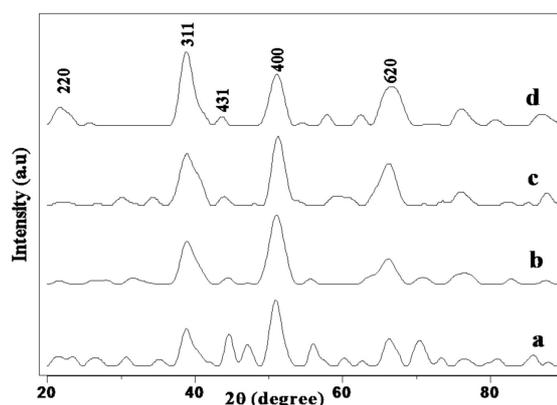


Figure - 1: XRD pattern of series of $Ni_xMg_{1-x}Fe_2O_4$ (a) $x=0.8$ (b) $x=0.6$ (c) $x=0.4$ (d) $x=0.2$ calcined at 550°C.

The highly intense and sharp peaks are present at $2\theta = 38, 41, 44.20, 50.68, 66.39$ from the reflection planes indexed as (220) (311) (431) (400) (620) respectively indicates the cubic structure of Ni-Mg ferrites. The X-ray diffraction pattern when compared with standard data (ICPDS PDF card no 00-008-0234) also confirms the formation of cubic Ni-Mg ferrite.

The lattice parameter 'a' of Ni-Mg ferrites are given in Table 1 which are in close agreement with standard data (8.34Å) [13]. The size of crystallite was evaluated by measuring the FWHM of the most intense peak (311) mentioned in table 1. Using the Debye Scherrer's formula [14] the

mean crystalline size of the sample lies in the range of 28-45 nm.

Table - 1: XRD analysis of Ni-Mg Ferrite samples

Sample	Crystallite size (nm)	Lattice constant A°
x = 0.8	45.13	8.4412
x = 0.6	36.38	8.4412
x = 0.4	28.05	8.4412
x = 0.2	40.19	8.4412

3.3. FT-IR analysis

The FT-IR spectra of series of Ni-Mg ferrites using dry KBr as a standard reference lies in the range of 4000-500 cm^{-1} are shown in figure 2. From the IR spectrum, it is observed that in each sample (a-d) the broad peak is present in the range 3200-3500 cm^{-1} which is due to the hydroxyl group adsorbed on the surface of catalyst, similarly in all the cases the peak in the range of 1500-1600 and 1380-1460 cm^{-1} is due to the deformation of the surface hydroxyl groups [15]. In the range from 1000-400, two main metal-oxygen bands are seen in IR spectra of all samples. The higher one generally observed in the range 600-550 cm^{-1} is caused by the stretching vibrations of the tetrahedral metal-oxygen bond ($M_{\text{tetra}}\text{-O}$). The lowest band usually observed in the range 450-400 cm^{-1} is caused by the metal oxygen vibrations in the octahedral sites ($M_{\text{octa}}\text{-O}$) [16].

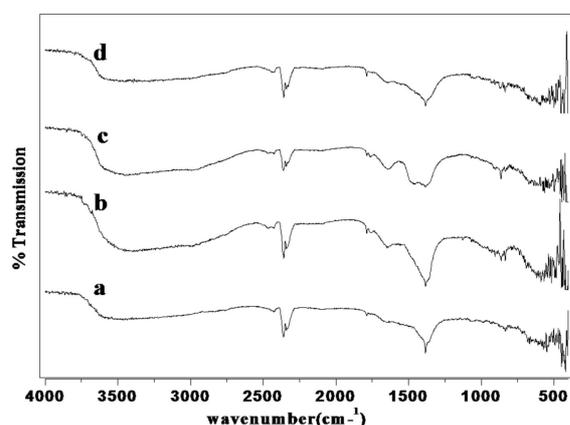


Figure - 2: FT-IR spectra of (a) x = 0.8, (b) x = 0.6, (c) x = 0.4, (d) x=0.2 Ni-mg ferrite calcined at 550°C.

3.4. SEM and EDS analysis

The surface morphology of the synthesized Ni-Mg Ferrite is studied by scanning electron micrograph and shown in figure 3. The SEM micrograph of Ni-Mg ferrite catalyst shows agglomeration of particles and irregular in shape. The as prepared samples have spongy and fragile network structure with voids and pores.

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis, an EDS spectrum of sample is shown in figure 4.

EDS pattern obtained for all the samples which gives the elemental composition in the samples. Table 2 shows the elemental composition of Ni-Mg Ferrite samples. The compound shows the presence of Ni, Mg, Fe and O.

Table - 2: Elemental composition of Ni-Mg Ferrite

Catalyst	Mass %				Total
	Ni	Mg	Fe	O	
X = 0.8	18.31	2.01	47.09	32.59	100
X = 0.6	13.96	3.65	49.53	32.86	100
X = 0.4	9.87	6.95	51.25	31.93	100
X = 0.2	4.93	9.03	54.19	31.85	100

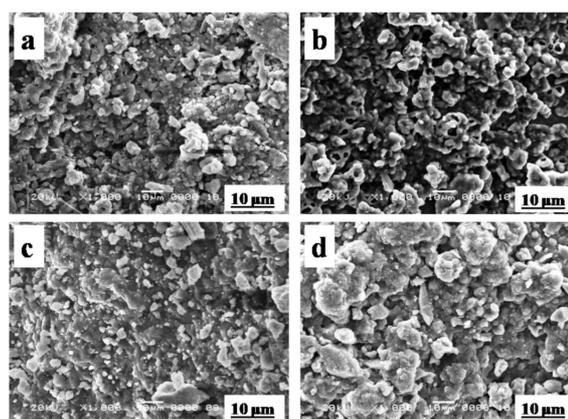


Figure - 3: SEM images of $\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ (a) x = 0.8 (b) x = 0.6 (c) x = 0.4 (d) x=0.2.

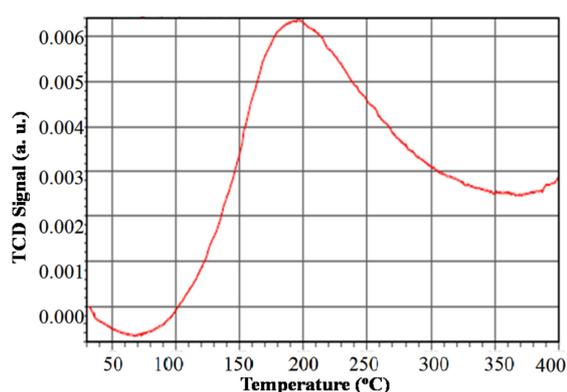


Figure - 4: NH_3 -TPD curve for TCD signal (a. u.) vs. Temperature $^\circ\text{C}$ of the sample $\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$.

3.5. BET and NH_3 -TPD analysis

NH_3 -TPD measurements were carried out by i) preheating 200 mg sample to 500 $^\circ\text{C}/\text{min}$ heating rate in helium with flow rate 20 cc/min . ii) adsorption of NH_3 at room temperature. iii)

desorption of adsorbed NH_3 with an heating rate $70^\circ\text{C}/\text{min}$ from room temperature to 550°C . The acidity of sample $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Fe}_2\text{O}_4$ was detected by temperature programme desorption of ammonia. Total acidity of Ni-Mg ferrite is 0.3763 mmol/g . BET theory aims to explain the physical adsorption of gas molecules on solid surface and serves as the basis for the measurement of the specific surface area of a catalytic material. The calculated BET surface area of Ni-Mg ferrite is $1.6665 \text{ m}^2/\text{g}$.

3.6. Catalytic activity results

In order to investigate catalytic activity for various compositions of Ni-Mg Ferrites, the typical reaction of benzaldehyde and malononitrile was carried out using the different compositions of Ni (II) and Mg (II) (Table 3). It is observed that, the $\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ have better catalytic activity. In order to get best possible experimental results, the typical reaction of benzaldehyde and malononitrile was carried out by varying catalyst amount (Table 4) and also in different solvents (Table 5). From the results obtained, it is observed that 0.2 gm synthesized Ni-Mg Ferrite was most effective in water which affords 90% yield of the product where as CH_3CN affords lower yield. The reaction was carried out in THF, Toluene, CH_2Cl_2 and ethanol, all failed to yield product. The same reaction was carried out in the absence of catalyst but reaction did not yield product even after 30 minutes, however, when the same reaction was carried out in the presence of synthesized catalyst, product was formed with excellent yield indicates the role of used catalyst, by way of providing required surface area to effect the reaction.

Table - 3: Knoevenagel reaction of benzaldehyde, malononitrile catalyzed by different proportion of Ni and Mg in Ferrite as a catalyst^a.

Entry	Catalyst	Time (min)	Isolated yield ^b (%)
1	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	90
2	$\text{Ni}_{0.6}\text{Mg}_{0.4}\text{Fe}_2\text{O}_4$	15	72
3	$\text{Ni}_{0.4}\text{Mg}_{0.6}\text{Fe}_2\text{O}_4$	15	65
4	$\text{Ni}_{0.2}\text{Mg}_{0.8}\text{Fe}_2\text{O}_4$	15	60

^aReaction condition: benzaldehyde (5mmol) and malononitrile (5mmol), Ni-Mg Ferrite 0.2 gm, 20 ml water as solvent, stirred 15 min. ^bIsolated yield.

The recovery and reusability of the catalyst was also examined as this is important from an industrial point of view. The catalyst was separated, washed with ethyl acetate, dried at 60°C and activated at 120°C for 1hr before the next catalytic run. The reusability of the catalyst was investigated for the reaction of 4-chloro

benzaldehyde with malononitrile and it could be re-cycled five times without any loss of activity in this case also the yields were excellent (Table 6). Using these optimized reaction conditions, the one-pot Knoevenagel condensation reaction of the various aldehydes and malononitrile were investigated and results are shown in table 7. A variety of differently substituted aromatic aldehyde possessing electron donating (CH_3 , OCH_3 , OH) and electron withdrawing groups (NO_2) gave good yields (90%-94%) and reactions were completed within 15-20 minutes in water.

Table - 4: Optimization of the amount of synthesized Ni-Mg Ferrite as catalyst for Knoevenagel reaction^a

Entry	Ni-Mg Ferrite	Time (min)	Isolated Yield ^b %
1	None	30	Trace
2	0.1	15	73
3	0.2	15	90
4	0.3	15	90

^aReaction condition: benzaldehyde (5mmol) and malononitrile (5mmol), Ni-Mg Ferrite, 20 ml water as solvent, stirred 15 min. ^b Isolated Yield

Table - 5: Synthesized Ferrite catalyzed Knoevenagel condensation of Benzaldehyde, malononitrile in different solvents^a

Entry	Solvent	Isolated Yield ^b %
1	EtOH	40
2	CH_3CN	30
3	Toluene	0
4	THF	0
5	CH_2Cl_2	0
6	H_2O	90
7	None	0

^aReaction condition: benzaldehyde (5mmol) and malononitrile (5mmol), Ni-Mg Ferrite 0.2 gm, 20 ml solvent, stirred 15 min. ^b Isolated Yield.

Table - 6: Recycle and reusability of $\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$ ^a

Entry	Ni-Mg Ferrite	Time (min)	Isolated Yield ^b %
1	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	90
2	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	90
3	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	88
4	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	86
5	$\text{Ni}_{0.8}\text{Mg}_{0.2}\text{Fe}_2\text{O}_4$	15	86

Reaction condition: 4-chlorobenzaldehyde (5mmol) and malononitrile (5mmol), Ni-Mg Ferrite 0.2 gm, water as solvent 20 ml, stirred 15 min. ^b Isolated Yield.

Table - 7: Synthesized Ni-Mg Ferrite catalyzed Knoevenagel reaction of aromatic aldehydes and malononitrile^a.

Entry	R	Time (min)	Isolated Yield ^b (%)	M. P. (°C)	
				Found	Reported
3a	H	15	90	81-83	82-84 ¹⁷
3b	4-CH ₃	20	88	132-133	134-135 ¹⁸
3c	4-NO ₂	15	97	158-159	159-160 ¹⁷
3d	4-OCH ₃	20	85	112-113	113-114 ¹⁸
3e	4-Cl	15	90	161-162	161-163 ¹⁷
3f	4-OH	20	90	185-187	187-188 ¹⁷
3g	3-NO ₂	15	95	103-105	103-105 ¹⁹
3h	2-Cl	20	92	93-94	92-94 ²⁰

^aReaction condition: aromatic aldehyde (5mmol) and malononitrile (5mmol), Ni-Mg Ferrite 0.2 gm, 20 ml water as solvent, stirred. ^bIsolated Yield.

4. CONCLUSION

In the present synthesis and characterization of series of Ni_xMg_{1-x}Fe₂O₄ with x = 0.8, 0.6, 0.4 and 0.2 has been systematically developed in order to find out the best possible catalytic activity. We have developed a novel, eco-friendly and efficient method for Knoevenagel condensation. The products were obtained in short time periods by using Ni-Mg Ferrite as a catalyst under very mild reaction conditions at room temperature. The use of an inexpensive medium, the rapid completion of reaction, and the high yield of product are all advantages of the present method.

Acknowledgement

We are grateful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004 (MS), India for providing the laboratory facility.

5. REFERENCES

- Borhade SR and Waghmode SB. Studies on Pd/NiFe₂O₄ catalyzed ligand-free Suzuki reaction in aqueous phase: synthesis of biaryls, terphenyls and polyaryls. **Beilstein J. Org. Chem.** 2011; 7: 310.
- Delpiero G, Trifiro F and Vacari A. Non-stoichiometric Zn-Cr spinel as active phase in the catalytic synthesis of methanol. **J. Chem. Soc. Chem. Commun.** 1984; 10: 656.
- Pradeep A, Priyadharsini P and Chandrasekaran G. Sol-gel route of nano particles of MgFe₂O₄ and XRD, FTIR and VSM study. **J. of Magn. Mag. Mater.**, 2008; 320: 2779.
- Jones G. The Knoevenagel condensation reaction in organic reactions. **Inorganic Reaction, Wiley**, New York, Volume 15: 204 1967.
- Reeves RL and Patai S. The Chemistry of carbonyl compounds. **Interscience publishers**, New York, 567 1996.
- Tietze LF, Beifuss U, Trost BM, Fleming I and Heathcock CH. comprehensive organic. **synthesis pergamon press**, oxford Volume 2: 341 1991.
- Martin CA and Aranda RM. Application of solid base catalysts in the preparation of prepolymers by condensation of ketones and malononitrile. **Appl. Catal. A** 1993; 105: 271-279.
- Tietze LF. Domino reactions in organic synthesis. **Chem Rev.**, 1996; 96: 115.
- Harjani JR, Nara SJ and Salunkhe MM. Lewis acidic ionic liquids for the synthesis of electrophilic alkenes via the Knoevenagel condensation. **Tetrahedron Lett.**, 2002; 43: 1127.
- Attanasi O, Filippone, and Mei A. Effect of Metal Ions in Organic Synthesis. part XVI. Knoevenagel Condensations of Aldehydes and Tosylhydrazones with 2,4-Pentanedione by Copper (II) Chloride-Catalyzed Reaction. **Synth. Commun.** 1983; 13: 1203.
- Rao PS and Venkataratnam RV. Zinc chloride as a new catalyst for Knoevenagel condensation. **Tetrahedron Lett.**, 1991; 32 5821.
- Gupta R, Gupta M, Paul S and Gupta R. Silica Supported Ammonium Acetate: An Efficient and Recyclable Heterogeneous Catalyst for Knoevenagel Condensation between Aldehydes or Ketones and Active Methylene Group in Liquid Phase. **Bull. Korean Chem. Soc.** 2009; 30(10): 2419.
- Smith J and Wijn HPJ. Ferrite The Netherlands: **Philips technical library Eindhoven**, Netherlands, 137-1959.

14. Cullity BD. Elements of X-ray diffraction 2nd Ed., **Addison-Wesley**, California, 1978: 102.
15. Langashetty A, Havanoor V and Basavaraj S. Microwave-assisted route for synthesis of nanosized metal oxides. **Sci Technol. Adv .mater.** 2007; 8: 484.
16. Waldron RD. Infrared Spectra of Ferrites, **Phys.Rev.**, 1955; 99 : 1727.